

Projection method for rapid *ab initio* calculations of metals

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An improvement of the Energy Renormalization Group method is proposed for systems with small gap, based on the projection methods developed by H. Feshbach. It is tested for the ground state energy of the one-dimensional tight-binding model.

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I. INTRODUCTION

The key point in the construction of fast, $\mathcal{O}(N)$ numerical methods is the gap in the excitation spectrum above the ground state which renders the interactions short ranged. Systems without gap display infrared singular, long range interactions which slow down the convergence of the numerical algorithms. It seems natural to seek different strategies to deal with the short and the long range quantum fluctuations. In particular, one may use rapid numerical methods for the short range fluctuations and treat the more difficult long range sector with slower, more sophisticated method. Such a mixed numerical algorithm is discussed in this paper.

The strategy of the renormalization group¹ is a natural candidate for the construction of such an algorithm. In fact, the renormalization group is a systematic method to successively eliminate certain degrees of freedom or fluctuation modes in such a manner that their impact on the dynamics is accumulated in the effective theory which is constructed for the remaining degrees of freedom. The algorithm proposed in this paper consists of two steps. First, a rapid numerical method is applied for the elimination of the short range fluctuations. What is left is a dynamical problem of the long range fluctuations described by an effective Hamiltonian. This problem is dealt with in the second step of the algorithm by the diagonalization of the effective Hamiltonian.

The question of central importance for such a mixed method is the relation between the total dimension of the Hilbert space and the dimensionality of the linear space of the effective theory where the exact diagonalization is performed. Let us denote by \mathcal{E} an intrinsic energy scale of the system and introduce $N_>$ and $N_<$ as the number of modes with energy superior or inferior of \mathcal{E} . One may call $N_>$ and $N_<$ ultraviolet and infrared cut-off. Our algorithm will be $\mathcal{O}(N_>^2)$ but will slow down as $N_<$ is increased. Since $N_<$ grows with the size of the system in the absence of gap and remains finite when the gap is present our algorithm might be useful for systems with weak gap or truly gapless models of finite size. The numerical efficiency compared to other methods will be judged by the prefactor of $N_>$ in the required computer time so long the system size or the gap is kept fixed. We

believe that this prefactor will be rather small because the modes treated in this step are short ranged.

The traditional renormalization group method¹ consists of the repeated application of a three step procedure. The first step is the blocking, the elimination of certain variables from the system. This is usually achieved by the lowering of the ultraviolet cut-off, the highest energy the fluctuations may reach in the system. The second step is the construction of the effective theory for the remaining modes. Finally, in the third step which gave the name of the procedure, one performs a rescaling of the energy or other scales of the effective theory in order to restore the original ultraviolet cut-off. This last step is not always necessary.

There have already been a proposal in the literature for a partial implementation of this idea, the so called energy space renormalization group^{2,3}, realizing the blocking and the rescaling steps. In order to render this scheme systematical one can not be content with the naive elimination of the unwanted modes, the restriction of the Hamiltonian into a subspace, but should realize the second step as well, the accumulation of the effects of the excluded directions within the subspace retained. For this purpose we use a projection method developed in nuclear physics^{4,5,6}.

In sec. II, we expand the density matrix formalism, which is the fundament of *ab initio* algorithms. The locality principle and its use in linear-scaling methods are presented in sec. III. An exemple of such algorithm, the so called Fermi Operator Expansion is presented in section IV. In the last section we develop a Numerical Renormalization Group method in Hilbert Space around the Fermi level and propose an improvement inspired by projection method.

II. DENSITY MATRIX FORMALISM

In the framework of Density Functional Theory (DFT)^{7,8,9}, particularly in the Kohn-Sham scheme⁸, rapid *ab initio* calculation methods allowing linear scaling or near-linear scaling computation time have been developed recently^{10,11}. Most of the rapid *ab initio* algorithm is based on the one-particle reduced density matrix ρ which is assumed to be a projector on the subspace

spanned by the low-lying occupied states according to the *auf bau* principle :

$$\begin{aligned}\rho &= \sum_i f_{\infty,\mu}(\epsilon_i) |\psi_i\rangle\langle\psi_i| \\ &= \sum_{i=1}^{N/2} |\psi_i\rangle\langle\psi_i|\end{aligned}\quad (1)$$

where N denotes the number of electrons and $(\epsilon_i, |\psi_i\rangle)$ is an eigenfunction of the Kohn-Sham Hamiltonian H and f_β is defined as the Fermi-Dirac distribution function at the inverse temperature β ,

$$f_{\beta,\mu}(\epsilon) = \frac{1}{1 + e^{\beta(\epsilon - \mu)}}. \quad (2)$$

The form $H = \sum_i \epsilon_i |\psi_i\rangle\langle\psi_i|$ allows us to write the density matrix as

$$\begin{aligned}\rho &= f_{\infty,\epsilon_F}(H) \\ &= \Theta(\epsilon_F - H)\end{aligned}\quad (3)$$

Θ being the Heaviside function. The average energy and the particle number can be written as

$$E_{BS} = \sum_{i,j} \rho_{ij} H_{ji} \quad (4)$$

and

$$N = 2 \sum_{i,j} \rho_{ij} S_{ji} \quad (5)$$

where the density matrix is given in a localized orbital basis

$$\rho = \sum_{ij} \rho_{ij} |\phi_i\rangle\langle\phi_j| \quad (6)$$

and $H_{ij} = \langle\phi_i|H|\phi_j\rangle$, $S_{ij} = \langle\phi_i|\phi_j\rangle$.

III. PRINCIPLE OF "NEARSIGHTEDNESS"

This principle states^{12,13,14} that the matrix elements of the one-electron density matrix are negligible beyond the distance ca where a is the lattice spacing,

$$|i - j| > c \Rightarrow \rho_{ij} \simeq 0, \quad (7)$$

giving

$$E_{BS} \simeq 2 \sum_i \sum_{\max(0, i-c) < j < \min(N, i+c)} \rho_{ij} H_{ji}. \quad (8)$$

The decay of the density matrix ρ in real-space depends on the material. For systems with gap the decay is exponential^{12,13,14,15,16}

$$\rho(\vec{r}, \vec{r}') = e^{-\alpha|\vec{r} - \vec{r}'|} \quad (9)$$

where $\alpha \sim \sqrt{\Delta\epsilon_{gap}}$ for the tight-binding limit and $\alpha \sim a_{lattice} \cdot \Delta\epsilon_{gap}$ for the weak-binding limit. For systems with no gap the decay of ρ is algebraic at zero temperature^{16,17,18}

$$\rho(\vec{r}, \vec{r}') = k_F \frac{\cos(k_F|\vec{r} - \vec{r}'|)}{|\vec{r} - \vec{r}'|^2} \quad (10)$$

Such an algebraic decay reflects the presence of long range correlations and prevents linear-scaling in the numerical calculations. The electron states tend to be more localized for disordered systems and the matrix elements of the density matrix decay faster with the distance^{19,20}.

IV. FERMI OPERATOR EXPANSION

The polynomial expansion of ρ in Chebychev polynomials, the so called Fermi Operator Expansion^{21,22,23} is an important ingredient of rapid algorithms.

Chebychev polynomials are defined by the recursion formula

$$\begin{aligned}T_0(x) &= 1 \\ T_1(x) &= x \\ T_{n+2}(x) &= 2xT_{n+1}(x) - T_n(x)\end{aligned}\quad (11)$$

for $-1 \leq x \leq 1$. It is easy to see that actually $T_n(x) = \cos(n \arccos x)$. We use the functional form (3) in order to fit ρ with a Chebychev polynomials up to order p ,

$$\rho_\beta = f_{\beta,\mu}(H) \simeq \sum_{i=0}^p a_i(\beta_s, \mu_s) T_i(H_s) \quad (12)$$

where H_s is the dimensionless Hamiltonian scaled and shifted into the interval $[-1, 1]$,

$$\begin{aligned}H_s &= \frac{H - \bar{E}}{\Delta E} \\ \bar{E} &= \frac{1}{2}[\min(\text{spec}(H)) + \max(\text{spec}(H))] \\ \Delta E &= \frac{1}{2}[\max(\text{spec}(H)) - \min(\text{spec}(H))]\end{aligned}\quad (13)$$

and $\beta_s = \beta\Delta E$, $\mu_s = (\mu - \bar{E})/\Delta E$. The smallest and largest eigenvalue of H can be computed by using the Lanczos method which scales linearly with the size of the matrix. The projection coefficients

$$a_n(\beta_s, \mu_s) = \frac{2 - \delta_{n0}}{\pi} \int_0^\pi \cos(n\theta) \frac{1}{1 + e^{\beta_s(\cos\theta - \mu_s)}} d\theta \quad (14)$$

will be computed numerically by means of Fast Fourier Transform (FFT). The particle number conservation fixes the value of the Fermi energy level ϵ_F found by solving Eq. (6).

The accuracy of Fermi Operator Expansion can be estimates by recalling that one truncates the Chebychev polynoms T_n of Eq. (11) in such a manner that only the

matrix elements $(T_n(H))_{ij}$ with $|i - j| \leq c$ are retained. The computation time will be of order $pc^2N = O(N)$. It can be shown^{24,25} that the order of the Chebychev expansion should be

$$p \simeq \frac{2}{3}(d-1)\beta_s = \frac{2}{3}(d-1)\beta\Delta E \quad (15)$$

for the accuracy 10^{-d} of the expansion coefficients $\{a_i\}$. If the system has an HOMO-LUMO gap ΔE_{gap} and

$$\beta \geq \frac{2 \log_{10} d}{\Delta E_{gap}} \quad (16)$$

then

$$p \geq \frac{4(d-1)\Delta E \log_{10} d}{3\Delta E_{gap}}. \quad (17)$$

Since the range of correlations in the density matrix is bounded,

$$range(\rho) \leq p \, c \simeq \frac{2}{3}c(d-1)\beta\Delta E \quad (18)$$

the correlations grows with the inverse temperature for gapless systems and the linear-scaling methods are rendered inapplicable.

V. ENERGY RENORMALIZATION GROUP

We present now a renormalization group method in the energy space in order to treat systems with small gap. In the original version of this method^{2,3} one starts with a series of inverse temperatures $\beta_n \rightarrow \infty$ and the corresponding density matrices ρ_n which tend to be concentrated around the Fermi level as $n \rightarrow \infty$. This alone would not represent any improvement as far as the numerical difficulties of obtaining the density matrices are concerned. But the density matrices are constructed in decreasing subspaces $\mathcal{H}_n \supset \mathcal{H}_{n+1}$ where \mathcal{H}_{n+1} is span by the eigenvectors of ρ_n with large eigenvalues.

This algorithm is modified in order to implement the blocking in energy space. First a common chemical potential is introduced for each temperature which is adjusted at the end of the computation to dial the desired particle number. This modification is needed to clear the way for the blocking. The Hamiltonians were simply truncated in the original algorithm as their subspaces were restricted. In order to retain the dynamics of the excluded dimensions we employ a method developed in Nuclear Physics⁴ which yields an exact, $\mathcal{O}(N^2)$ algorithm.

A. Blocking in the Hilbert space

A geometric series of inverse temperatures $\beta_n = q^n \beta_0$ is introduced for $q > 1$ together with the corresponding

density matrices $\rho_{n,\mu} = f_{\beta_n,\mu}(H)$. The zero temperature expectation value of an observable A is written as a telescopic series

$$\langle A \rangle = \text{Tr}(\rho_{\infty,\mu} A) = \sum_n \text{Tr}(\Delta_{n,\mu} A). \quad (19)$$

where

$$\Delta_{n,\mu} = \rho_{n,\mu} - \rho_{n-1,\mu}, \quad \Delta_{0,\mu} = \rho_{0,\mu}.$$

Each term in this equation corresponds to a more restricted energy subspaces centered at the Fermi energy level as n is increased. The localization in the energy leads to delocalized states in real space in the absence of disorder. The ground state is approached by the telescopic summation by zooming onto the Fermi level and the corresponding density matrix projects on more and more extended states.

The order of the Chebychev expansion p is chosen to be independent of n and the coefficients obtained by FFT are

$$a'_m(\beta_n, \mu) = \langle \Delta_{n,\mu}, T_m \rangle \quad (20)$$

where

$$\Delta_{n,\mu} = f_{\beta_n,\mu}(H_n) - f_{\beta_{n-1},\mu}(H_n). \quad (21)$$

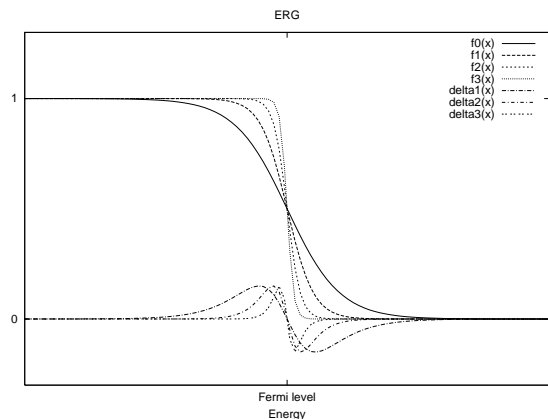


FIG. 1: Spectral representation of ρ_n and Δ_n .

B. Fixed-point

The convergence of the telescopic series can be expressed as the existence of a fixed point of the blocking in the energy space for energy dependent operators. In fact, let us suppose that a continuous operator A is commuting with the Hamiltonian H and can be diagonalized in a basis of eigenvectors of H . We can then express its

expectation value by means of ρ as

$$\begin{aligned}\text{Tr}(\Delta_{n+1,\mu}A) &= \int d\epsilon A(\epsilon)\Delta_{n+1,\mu}(\epsilon) \\ &= \frac{\beta_n}{\beta_{n+1}} \int d\epsilon A\left(\epsilon\frac{\beta_n}{\beta_{n+1}}\right)\Delta_{n,\mu}(\epsilon) \\ &= \frac{\beta_n}{\beta_{n+1}}\text{Tr}\left(\Delta_{n,\mu}A\left(\frac{\beta_n}{\beta_{n+1}}\right)\right)\end{aligned}\quad (22)$$

This expression allows us to rescale the operator A around the Fermi-level by the factor β_{n+1}/β_n and to keep $\Delta_{n,\mu}$ unchanged. Since A is a continuous operator the iteration of this step obviously leads to a fixed-point,

$$\text{Tr}(\Delta_{n+1,\mu}A) - \text{Tr}(\Delta_{n,\mu}A) \rightarrow 0 \quad (23)$$

as $n \rightarrow \infty$.

C. Projection

The identification of the subspaces proceeds by the construction of the projectors $P_n : \mathcal{H}_n \rightarrow \mathcal{H}_{n+1}$. We introduce first the following pseudo-projectors constructed by means of the Chebychev expansion

$$G_n = \frac{\partial \rho_{n,\mu}}{\partial \mu} = \beta_n \rho_{n,\mu} (1 - \rho_{n,\mu}) \quad (24)$$

Once the series $\{G_n\}$ is found another set of matrices $\{C_n\}$ is formed. The columns of C_n are basis vectors of \mathcal{H}_{n+1} by means of a heuristic version of the singular value decomposition with column pivoting^{2,3,26}. Since the dynamics of the excluded dimensions is retained in our case this choice is a less sensitive step of the algorithm then in the original version and influences the sparsity of the resulting density matrices only. As the next step, the overlap matrices $S_n = C_n^* C_n$ are constructed. Finally, the projectors are given as $P_i = C_i S_i^{-1} C_i^*$. S_i^{-1} can actually be obtained as $S_i^{-1/2} = \lim_{k \rightarrow \infty} A_k$ by the help of the algorithm²⁷

$$\begin{aligned}A_k &= \frac{1}{2}(3A_k - A_k B_k A_k) \\ B_k &= \frac{1}{2}(3B_k - B_k A_k B_k)\end{aligned}\quad (25)$$

with $A_0 = -\sqrt{\alpha} \cdot \mathbb{1}$, $B_0 = -\sqrt{\alpha} \cdot S_i$ and $\alpha = 1/\max_{j,k} |(S_i)_{jk}|$. The projected Hamiltonian is of the form

$$H_{n+1}^{ERG} = S_n^{-\frac{1}{2}} C_n^* H_n C_n S_n^{-\frac{1}{2}} \quad (26)$$

Up to now we have excluded certain directions of the Hilbert space which are supposed to be less important from the point of view of the ground state dynamics. In order to perform the analogue of the Kadanoff-Wilson blocking we have to construct an effective Hamiltonian^{4,5}

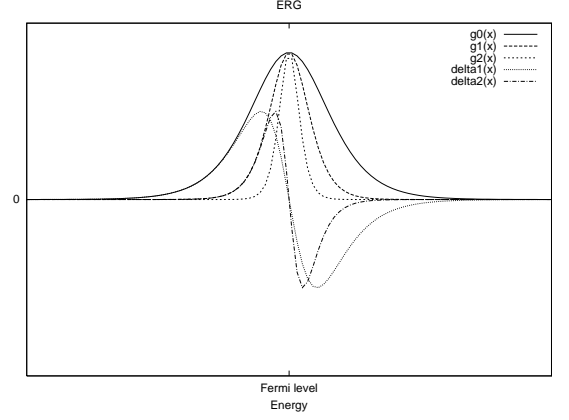


FIG. 2: Spectral representation of G_i and Δ_i .

H_{n+1} in the restricted space with the same dynamics around the Fermi level as those of H_n ,

$$\begin{aligned}H_{n+1} &= S_n^{-\frac{1}{2}} C_n^* \left(H_n + H_n Q_n \frac{1}{\mu - Q_n H_n Q_n} Q_n H_n \right) \\ &\quad \times C_n S_n^{-\frac{1}{2}} \\ &= H_{n+1}^{ERG} + S_n^{-\frac{1}{2}} C_n^* H_n Q_n \frac{1}{\mu - H_n Q_n H_n} Q_n H_n C_n S_n^{-\frac{1}{2}}\end{aligned}\quad (27)$$

where $Q_n = 1 - P_n$. The exclusion of directions from the Hilbert space renders the finding of the projection of the eigenvectors of the original Hamiltonian into the restricted space a nonlinear problem. This complication appears as a nonlinear dependence of the eigenvector equation in the restricted space on the eigenvalue. The energy eigenvalue was replaced by the Fermi level, μ , in the 'self-energy', the second term on right hand side of Eq. (27). The inverse in the right hand side can be obtained by the well-known *Schultz's* or *Hotelling's* method^{28,29,30} as $(\mu - H_n)^{-1} = \lim_{j \rightarrow \infty} X_j$ where

$$X_j = X_{j-1} [2\mathbb{1} - (\mu - H_n) X_{j-1}] \quad (28)$$

with the initial-guess³⁰ $X_0 = (\mu - H_n)^* / \sum_{j,k} (\mu - H_n)_{jk}^2$.

The calculation ends when the dimension of the subspace is sufficiently small for explicit diagonalization.

One can introduce approximations which render the method $\mathcal{O}(N)$. One possibility is the note that X_j of Eq. (28) converges quadratically and the order of 30 iterations, a value independent of the system size was always sufficient in our numerical test. Another possibility is based on the adjustment of the chemical potential at the end of the computation. This circumstance allows us to make the replacement

$$\frac{1}{\mu - Q_n H_n Q_n} \rightarrow \frac{1}{\mu} \quad (29)$$

in Eq. (27) where μ will include the 'average' of $Q_n H_n Q_n$ within \mathcal{H}_n . Such a simplification is more acceptable for large n where $\dim \mathcal{H}_n$ is not too large and the evolution is slow.

TABLE I: Relative errors of energy computations for different size of systems with $\beta_0 = 5$, $q = 10$ and with a Chebychev expansion $p = 10$

N	E_{Exact}	E_{ERG}	E_{HF}	$Error_{ERG}$	$Error_{HF}$	$Error_{ERG} - Error_{HF}$
256	93.39	95.44	91.58	2.20	1.94	0.26
384	139.90	142.95	139.09	2.18	0.58	1.60
512	186.41	190.47	186.61	2.18	0.10	2.07
640	232.93	237.98	234.12	2.17	0.51	1.66
768	279.44	285.50	281.63	2.17	0.79	1.38
896	325.95	333.01	329.15	2.17	0.98	1.19
1024	372.47	380.52	376.66	2.16	1.13	1.04
1152	418.98	428.04	424.17	2.16	1.24	0.92
1280	465.49	475.55	471.69	2.16	1.33	0.83
1408	512.00	523.06	519.20	2.16	1.41	0.75
1536	558.52	570.58	566.72	2.16	1.47	0.69
1664	605.03	618.09	614.23	2.16	1.52	0.64
1792	651.54	665.60	661.74	2.16	1.57	0.59
1920	698.05	713.12	709.26	2.16	1.60	0.55
2048	744.57	760.63	756.77	2.16	1.64	0.52

D. Numerical test

We considered a lattice of $2N$ sites in one dimension with nearest neighbor interaction described by the Hamiltonian³¹

$$H = 2 \sum_i a_i^+ a_i - \sum_{\langle i,j \rangle} a_i^+ a_j \quad (30)$$

at half filling. Being the simplest model for the conducting band electrons the matrix elements of the density matrix, computed in the appendix for half-filling, show metal-like decrease with the distance.

Table I shows the results of energy calculations with the algorithm of Eq. (27) for different sizes. It has been reported^{2,3} that the CPU time of the ERG method scales as $N \ln^2 N$. The computation of Eq. (27) which was done by applying the approximation (29) does not change this result since it contains matrix multiplications only.

VI. CONCLUSION

A new application of the renormalization group method is presented in this work. This method is designed to retain the dynamics of modes excluded from the computation and was developed for the path integral. But it is an ideal tool to improve systematically the truncations of the Hilbert space committed in the operator formalism, too. As an example the improvement of the Energy Renormalization Group was presented. Here the Kadanoff-Wilson blocking is performed in energy space and the effects of the directions of the Hilbert space lost by the truncation is retained. Therefore the dimension of the linear space is reduced but the physics which can be described by states within the reduced space remained the same. As long as the ground state and the low lying excitations are kept in the linear spaces constructed

in this sequence the salient features of the model can be described in a systematical and more economical manner.

The elimination of dimensions makes the eigenvalue equation nonlinear in the eigenvalues, an effect which is well known in many-body theory. In fact, say the self energy of a particle receives a complicated, energy dependent contribution from 'virtual', particle-number changing processes which leave from and return to the one-particle sector of the Fock space. We employed a widely used approximation which becomes exact for the ground state and the low lying excitations, the replacement of the energy eigenvalue by the Fermi level in the self-energy. The computational need of the resulting method is $\mathcal{O}(N_{>}^2)$ with a prefactor which growth with the volume. Nevertheless we find this result remarkable since systems with small gap can safely be treated by exact diagonalization in a low dimensional subspace.

We employed a further simplification of the effective Hamiltonian in our numerical test. We replaced the part of the Hamiltonian which belongs to the eliminated directions and appears in the self-energy by a 'mean-operator' which is proportional to the identity. This approximation is supposed to become exact for the ground state and the low lying excitations of a Fermi-liquid. The method is $\mathcal{O}(N_{>} \ln^2 N_{>})$ when this simplification is used.

Our method was tested numerically in the case of the one dimensional tight binding model. The ground state energy improved and a reduction of its *error* by 25% was found compared to the original algorithm for $N = 2048$.

The main question left open by the present work is the dependence of the computational requirement on $N_{<}$, the physical size of the system, and the explorations of alternative approximations which ultimately speed up the algorithm in this respect.

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APPENDIX A: ONE-PARTICLE DENSITY MATRIX

This Appendix contains some details of the computation of the density matrix for the tight binding model of Eq. (30) at half filling.

The matrix of eigenvectors corresponding to the N lowest eigenvalues of H is given by

$$C_{\mu\nu} = \frac{1}{\sqrt{N + \frac{1}{2}}} \sin\left(\frac{\pi\mu\nu}{2N+1}\right). \quad (\text{A1})$$

for $1 \leq \mu \leq 2N$, and $1 \leq \nu \leq N$. The reduced density matrix

$$\rho = CC^* \quad (\text{A2})$$

is a projector with the diagonal matrix elements

$$\rho_{\mu\mu} = \frac{1}{2}. \quad (\text{A3})$$

If μ and ν have same parities, i.e $\mu - \nu$ is even then $\rho_{\mu\nu} = 0$. For $\nu = \mu + 2k + 1$

$$\rho_{\mu\nu} = \frac{1}{4N+2} \left[\frac{(-1)^k}{\sin \frac{\pi}{2} \frac{2k+1}{2N+1}} - \frac{(-1)^{\mu+k}}{\sin \frac{\pi}{2} \frac{\mu+k+\frac{1}{2}}{2N+1}} \right]. \quad (\text{A4})$$

In order to find rate of decrease of $\rho_{\mu\nu}$ we consider the limit $N \rightarrow \infty$ but keep $\nu - \mu = 2k$ fixed,

$$\rho_{\mu,\mu+2k} \approx \frac{(-1)^k}{2k\pi}. \quad (\text{A5})$$

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¹ K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975)

² R. Baer and M. Head-Gordon, J. Chem. Phys. **109**, 10159 (1998)

³ R. Baer and M. Head-Gordon, Phys. Rev. B **58**, 15296 (1998)

⁴ H. Feshbach, Annals of Physics, **19**, 287-313 (1962)

⁵ J. Rau, cond-mat/9607198, (1996)

⁶ J. Muller, J. Rau, Phys. Lett. B **386** (1996) 274

⁷ P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964)

⁸ W. Kohn and L. J. Sham, Phys. Rev. B **140**, 1133 (1965)

⁹ K. Capelle, cond-mat/0211443, (2003)

¹⁰ S. Goedecker, Rev. Mod. Phys. **71**, 1085 (1999)

¹¹ S. Y. Wu, C. S. Jayanthi, Phys. Rep. **358**, 1 (2002)

¹² W. Kohn, Chem. Phys. Lett. **208**, 167 (1993)

¹³ J. des Cloizeaux, Phys. Rev. **135**, (1964); ibid (1964) A698

¹⁴ W. Kohn, Phys. Rev. **115**, 809 (1959)

¹⁵ W. Kohn, Int. J. Quart. Chem. **56**, 229 (1995)

¹⁶ S. Ismail-Beigi, T. Arias, Phys. Rev. Lett. **82**, 2127 (1999)

¹⁷ S. Goedecker and O. Ivanov, Solid State Commun. **105**, 665 (1998)

¹⁸ S. Ismail-Beigi, T. Arias, Phys. Rev. Lett. **82**, 2127 (1999)

¹⁹ W. Kohn, Phys. Rev. Lett. **21** (1968) 13

²⁰ W. Kohn, Phys. Rev. Lett. **76** (1996) 3168

²¹ S. Goedecker and L. Colombo, Phys. Rev. Lett. **73** (1994) 122

²² S. Goedecker, J. Comp. Phys. **118**, 261 (1998)

²³ S. Goedecker and M. Teter, Phys. Rev. B **51**, 9455 (1995)

²⁴ R. Baer and M. Head-Gordon, Phys. Rev. Lett. **79** (1997) 3962

²⁵ R. Baer and M. Head-Gordon, J. Chem. Phys. **107**, 10003 (1997)

²⁶ G. H. Golub and C. F. Van Loan, *Matrix computations*, 3rd ed., (John Hopkins University Press, Baltimore, 1996), p. 591

²⁷ V. B. Larin, Technicheskaya Kibernetika **1**, 210 (1992)

²⁸ W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in C++, 2nd ed.*, 2001, p. 60

²⁹ A. S. Householder, *The theory of matrices in numerical analysis*, Dover Publications, Inc. New-York, 1975, p. 94

³⁰ V. Pan, and J. Reif, *Proceedings of the Seventeenth Annual ACM Symposium on Theory of Computing*, 1985

³¹ P.W Atkins and R.S Friedman, *Molecular Quantum Mechanics*, 3rd ed., (Oxford University Press, 1997), p. 267